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Nitriding in cathodic cage of stainless steel AISI 316: Influence of sample position

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ABSTRACT

Cathodic cage plasma nitriding is a new growth technique based on multiple hollow cathode effects. The samples are kept at a floating potential inside a cage that acts as a cathode and shields the samples from the cathodic potential. The aim of this work is to perform a systematic study of the properties of nitrided layers as a function of the distance from the nitriding sample surface to the cage wall using this technique. Cylindrical austenitic stainless steel AISI 316 samples were placed in different positions on an alumina plate inside the cathodic cage. The nitrided samples were characterized by optical microscopy, X-ray diffraction and microhardness measurements. The results show that the temperature inside the cage is nearly uniform and that the nitrided layers possess good physical properties and uniformity. Therefore, the differences in the nitrided layer thicknesses obtained at different positions must be due to particle flow reaching the sample surface, depending on how far the sample is from the cage walls.

1. Introduction

All types of stainless steel are of great use in engineering due to their high corrosion resistance, although they possess low wear resistance and reduced hardness. These two last properties are significantly improved through ionic plasma nitriding [1–3]. As is well known, when the nitriding of austenitic stainless steel is carried out at temperatures higher than 723 K, layers having high wear resistance and surface hardness are produced, while the corrosion resistance diminishes significantly due to precipitation of chromium nitrite, with a consequent reduction of the chromium content in the matrix. In contrast, when the nitriding is carried out at temperatures lower than 723 K a phase supersaturated with nitrogen, called expanded austenitic or S-phase, which possesses high hardness and wear resistance as well as a great resistance to corrosion, is formed [4,5].

In this study the objective is to identify the influence of the nitriding sample position inside the cathodic cage on the nitriding layer properties. Cathodic cage plasma nitriding is a new technique, based on the hollow cathode effect due to the plasma confinement in each hole of the cage, on which the samples are placed on an isolating plate and surrounded by a metallic cage assembled with holes (Fig. 1).

Using this technique, we intend to obtain nitrided layers with microhardness and corrosion resistance as good as those of layers obtained by conventional ionic plasma nitriding, but with some improvements, such as greater thickness, better uniformity, higher hardness and the elimination of the so-called border effect [6–8].

2. Materials and methods

The material used in this study was annealed austenitic stainless steel 316 (microhardness 240 HV), provided by Villares Metals SA. Its nominal elemental atomic composition is shown in Table 1.

The previously annealed austenitic stainless steel AISI 316 samples were machined in cylindrical form, ground with 320, 400, 600 and 1200 mesh grinding papers and polished on a felt disc with 0.3 and 1 μm diamond suspensions. They were then ultrasonically cleaned in an acetone bath, before being placed in the nitriding chamber. The nitriding system consists of a power source (maximum tension 1500 V, current 2 A) and a cylindrical stainless steel vacuum chamber (40 cm in diameter and 40 cm in height). We used a cathodic cage made from stainless steel 316 of thickness 0.8 mm, diameter 112 mm, and height 25 mm, width 8 mm diameter holes uniformly distributed, with a distance of 9.2 mm between centres of adjacent holes. With this configuration the plasma is formed on the cathodic cage, which works as the cathode, and not directly on the surface of the samples [6,7].

The samples were pre-treated with hydrogen for 20 min at a temperature of 573 K and a pressure of 200 Pa in order to

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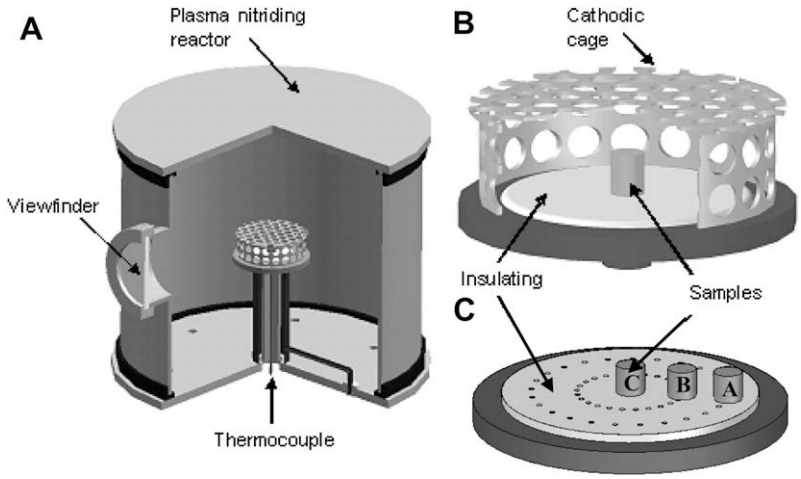

Fig. 1. (A) The reactor scheme of plasma ionic nitride, (B) configuration of cathode cage used onto process and (C) spatial distribution of the samples nitrided at 250 Pa.

Table 1
Elemental composition of the austenitic stainless steel AISI 316 (at.%).

Cr	Ni	Mo	C	Mn	Si	P	S	Al	Fe
16–18%	10–14%	2–3%	0.08%	2%	1%	0.04%	0.03%	0.02%	Balance

Table 2
Layer thicknesses and microhardness of the nitrided layers as a function of the work pressure and sample position inside the cage (5 h, 723 K and 80% $N_2 + 20\%$ H_2).

Pressure [Pa]	Sample position	Nitriding layer thickness [μm]	Microhardness $[HV_{0,1}] \pm 8.0\%$
250	A	28.2 ± 0.7	1115
	B	24.4 ± 0.8	1305
	C	22.2 ± 1.0	1213
120	A	61.9 ± 1.0	978
	B	56.7 ± 1.5	953
	C	51.4 ± 1.6	931

eliminate contaminants such as oxides and/or grease/fat adsorbed on the surface. They were then treated under the following conditions: 5 h at a temperature of 723 K at pressures of 120 and 250 Pa in nitriding atmosphere mixture of 80% N_2/20% H_2, with a flow rate of 20 sccm, regulated with a mass flow controller. After the nitriding process, the samples were cooled down slowly inside the chamber to a temperature of 353 K to prevent oxidation. Then they were prepared for metallography analysis and etched in a solution containing 50% HCl + 25% HNO_3 + 25% H_2O and Beraha II.

The composition and texture of the samples were analyzed using X-ray diffraction (XRD). These analyses were carried out using Cu Kα (wave length: 0.154 nm) and Mo Kα ($\lambda = 0.07094$ nm) lines operated at 40 KV using a Shimadzu XRD-6000 instrument. An optical microscope (Olympus BX60M) and SEM (Philips, model XL 30 ESEM) were used to observe and measure the thickness of the layers and to evaluate their texture and uniformity. Microhardness profiles of the top surface of the nitrided samples were measured, using an instrument Pantec 1000 with pyramidal indentor using load of 100 g, in order to evaluate the uniformity of the layers.

3. Results and discussion

The surface microhardness and layer thickness measurement data for samples treated in different positions (A, B and C –Fig. 1c), under pressures of 120 and 250 Pa, are presented in Table 2.

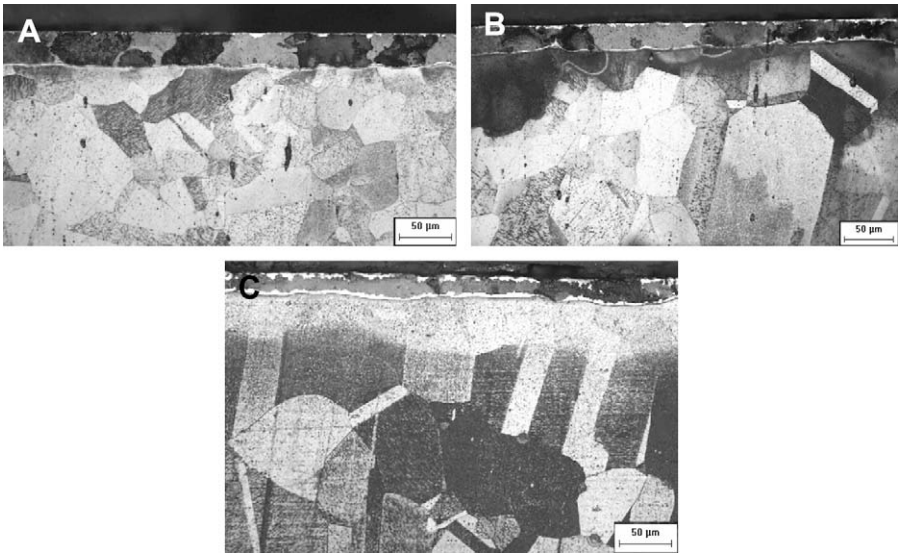

Fig. 2. Micrographs of samples treated under a pressure of 250 Pa at temperatures of 723 K during 5 h placed at different positions (A), (B) and (C).

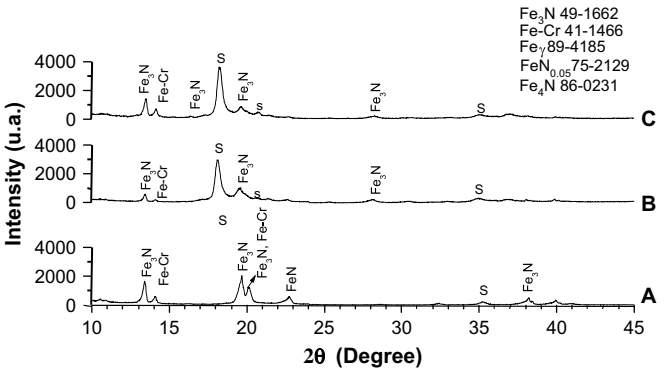

Fig. 3. X-ray diffractograms [Mo Kα ($\lambda = 0.07094$)] for samples nitrided at 723 K, during 5 h in a pressure of 250 Pa, placed at different positions (A, B, C) inside of the cathodic cage.

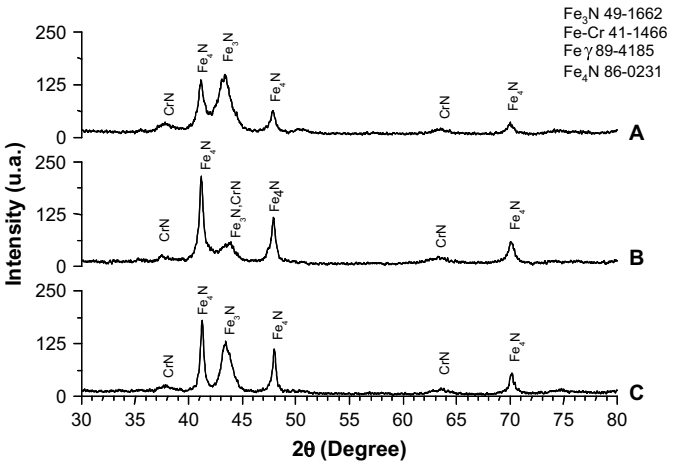

Fig. 5. X-ray diffractograms [Cu Kα (wave length: 0.154 nm)] for samples nitrided at 723 K, during 5 h under a pressure of 120 Pa, placed at different positions (A, B, C) inside of the cathodic cage.

These data show that samples treated by the cathodic cage technique under the low pressure (120 Pa) develop nitrided layers thicker than the samples treated at the pressure of 250 Pa, in agreement with previous works [6,7]. At a lower working pressure we have an increase in the mean free path of the ion particles that reach the holes of the cathodic cage walls, increasing the sputtering rate, and consequently the particle flow, and obtaining higher deposition efficiency, resulting on thicker layers than those obtained from conventional ionic nitriding. This confirms that, in the cathodic cage technique, which is based on the hollow cathodic effect, deposition is the predominant process.

In the present technique, species once deposited on the sample surface are not subsequently sputtered from it. This contrasts with the case of conventional ionic plasma nitriding in which there is a competition between sputtering from the sample surface and diffusion. In the conventional technique, for a nitriding temperature of 623 K, the sputtering rate is 1.62 μm/h [10]. Thus nitriding for 5 h results in a layer of 8.10 μm thinner than that obtained using the cathodic cage technique. For temperatures of 723 K and 873 K the sputtering rate from the sample is 3.0 μm/h [11], so that on nitriding for 5 h the thickness difference is 15.0 μm.

The present results (Table 2) show that there is a slight increase in the layer thicknesses for the samples placed in positions nearer to the cage walls (positions B and C) due to the higher species flow rate, produced by the superposition of the species flow from the top and lateral cage walls.

The micrographs for the samples nitrided under a pressure of 250 Pa (Fig. 2) show some differences, especially when we compare the layer formed in the sample placed on the position C with the others. For the sample placed at position C, the micrograph shows white regions at the interface of the deposited layer with the substrate and at the layer surface. This is an indication of the presence of the S-phase [4,5,9,14–17]. The other samples do not show such pronounced regions.

The X-ray diffractograms presented in Fig. 3 show that for the case of thicker nitrided layers (positions A, near the edge of the sample table) there is a predominance of iron nitrides [12]. This is due to the fact that the nitriding species, which originate in the cathodic cage walls reach the sample surface with larger energy and intensity than in the case of the samples nearer to the centre of the sample table.

The micrographs presented in Fig. 4 show that, for the samples treated under the pressure of 120 Pa, the nitrided layers do not present white regions at the layer/substrate interface and at the layer surface, in contrast with the samples nitrided under a pressure of 250 Pa. This shows that the expanded austenitic is absent, and is confirmed by the X-ray analysis (Fig. 5). The absence of the S-phase is probably responsible for the systematic reduction in the surface hardness (Table 2) when compared with the samples treated at a pressure of 250 Pa.

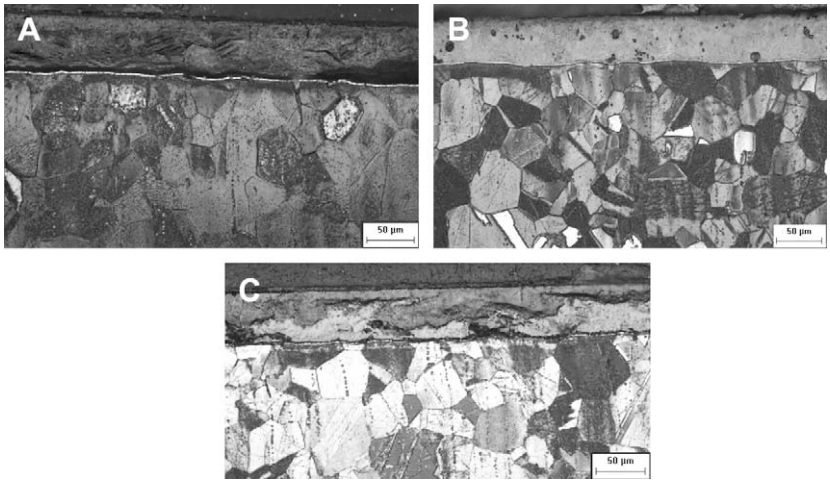

Fig. 4. Micrographs of samples treated under pressure of 120 Pa at the temperatures of 723 K during 5 h placed at different positions (A), (B) and (C).

The X-ray diffractograms presented in Fig. 5, for a pressure of 120 Pa, do not present intensity variation of the peaks characteristic of iron nitride [γ'-Fe_4N]. This is an indication that a thermal gradient in the interior of the cathodic cage is insignificant, since any increase in the treatment of temperature should cause an increase of the intensity of the iron nitride peaks, γ'-Fe_4N [13].

4. Conclusions

We have shown that the cathodic cage technique is efficient for the growth of uniform, resistant, hard, thick layers for any spatial distribution of samples. Since the technique is based on a multiple hollow cathode process, we have established most suitable treatment process parameters for effective growth.

Samples nitrided at lower pressure (120 Pa) present thicker nitrided layers and lower hardness than the samples nitrided at 250 Pa. Moreover for samples nitrided under the same working pressure, but placed at different positions inside the cathodic cage, the nitrided layers are thicker for samples nearer to the cage.

Acknowledgements

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